Preliminary experiments on filament winding nylon impregnated glassfibers (FIT)

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Abstract.

Some preliminary experiments have been conducted on the FIT material, which are nylon pre-impregnated glass-fibres. The advantages of this type of material are mainly focussed on manufacturing technology. Filament-winding, flexible braids and weaves are some of the possibilities.

This report gives a characterization of the material with respect to the basic properties of the material. Some filamentwinding experiments will be described with regard to a number of important parameters.
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1. **Introduction.**

The application of high performance thermoplastics as a ductile matrix material in composite-technology is increasing. The advantages which these thermoplastics have to offer are beginning to become well known to material users. Various systems featuring aramid-, carbon- and glass fibres are commercially available now. These systems consist mostly of pre-impregnated weaves or UD-tapes which need to be stacked, heated and pressed to produce a laminate. Some manufacturers do offer pre-consolidated sheet-material on which various forming methods can be applied.

However, the stiffness of pre-consolidated sheets implies certain constraints on the possibilities of some forming methods. For instance, strongly curved parts can best be formed using hot/cold-mould techniques, (eg. a mould which can be heated and cooled in very short periods of time). If a flexible weave should exist, this material can then easily be draped in the cold mould and consequently heated, pressed and cooled again. Hence, the need for TP-impregnated (flexible) high performance rovings is obvious. Such a roving will not only offer the possibilities of producing flexible weaves, but also braiding-, filament-winding- (non-geodetical!) and even knitting-techniques are possible.

Several options are feasible to obtain a flexible roving, containing enough thermoplastic resin for a reasonable impregnation. Melt- or solution impregnation of a single bundle of fibres, hybrid yarns are some of the possibilities. ATOCHEM (France) has managed to produce a 'thermoplastic' fibre using a powder- and extrusion technique (Fibre Impregné Thermoplastique: FIT). Preliminary products were aramid fibres impregnated with PA-12, but a large production has been started using various grades of nylon and glass fibres. The TU-Delft has received a number of bobbins of this new material in order to investigate the properties and the possibilities which these fibres have to offer.

This report gives a characterization of the diverse grades of FIT-material and discusses some preliminary filament-winding-experiments.

2. **The FIT material.**

The FIT-material consists of a bundle of glass fibres which have been treated with the powder impregnation technique. At present, very fine powder grades (8 to 20 microns size) of high performance thermoplastics have been developed. Basically the powder-method consists of spreading the fibres, charging it electrostatically and then passing it through a bath containing the thermoplastic powder particles. After reconstituting the filaments, this roving (which now contains a certain amount of the powder particles) is coated with a thin layer of nylon by an extrusion process. This tube allows the roving to maintain its intrinsic flexibility without the hazard of losing the powder. Furthermore, the total resinweight percentage can be exactly adjusted to a desired amount by varying the thickness of the extruded tube. ATOCHEM has used various combinations of nylon for the tube and the powder. The different types of the obtained material are summarized in table 1.
Table 1: The combinations of glassfibres and nylon.

<table>
<thead>
<tr>
<th>Type of nylon (powder/tube)</th>
<th>glass-fibre (Tex)</th>
<th>name</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA-12/PA-12</td>
<td>320</td>
<td>FIT 320/12</td>
</tr>
<tr>
<td>PA-12/PA-12</td>
<td>1200</td>
<td>FIT 1200/12</td>
</tr>
<tr>
<td>PA-6/PA-11 (V3)</td>
<td>320</td>
<td>FIT 320/6/11</td>
</tr>
</tbody>
</table>

One combination (FIT 320/6/11) is quite unlikely to be viable for further application due to the different meltingpoints of the two grades of nylon, PA-6 \( T_m = 226^\circ C \) and PA-11 \( T_m = 184^\circ C \), which are used for the powder and tube respectively. This means that the required temperature for melting the powder lies far beyond the meltingpoint of the tube. As a result the PA-11 tube will degrade (oxidize) due to the excessive heat resulting in a brown color of the product.

A conversed combination (e.g. PA-6 for the tube and PA-12 as powder material) would be more logical. In that case the above mentioned effect will not occur and furthermore the heat, necessary for melting the tube will probably be enough for an adequate heating of the powder inbetween the glassfibres. This can even be preferable because it has been observed during experiments with the FIT 320/12 that the total heatflux necessary for melting the whole fibre (in particular the powder) has an oxidizing effect on the outer surface of the fibre, thus resulting in a brown color of the product. This phenomenon occurred using the hot air heating method which will be discussed later.

**Fibre volume content.**

An important parameter of compositesmaterials is the fibre volume percentage. By subtracting the weight of the glassfibres (given by the tex-value: g/1000 m) from the total weight of a piece of an impregnated fibre the amount of nylon (per meter) can be determined. Using the specific weights of the diverse components the specific weight and fibre volume percentage of the material can be determined.

Another approach of determining the specific weight of the material is using the dry-wet weighting method. However, due to the method of manufacturing of the FIT-material a certain amount of air is locked in. This will inhibit the application of the dry-wet weighting method.

The air in the fibres gives rise to another major problem, in particular the inclusion of air in the prepared product. Earlier tests have shown that this will happen to a great extent.\(^{12,41}\) This phenomenon will be discussed later.

In accordance with the above, the fibre volume percentage is determined. A number of specimen has been weighted using an analytical balance.
Because the results appeared to be quite irregular, 10 meter FIT 320/6/11 has been cut in 10 parts and the weight of each part has been determined. As can be seen from Fig.1, a significant variation in weight per meter occurs (18.4%), even on short distances.

| 1.01 | 1.08 | 1.06 | 0.98 | 1.02 | 1.06 | 1.06 | 0.98 | 1.13 | 1.06 |

Fig.1: Variations in weight (g/m) of the FIT 320/6/11 material.

From resin burn-off tests (3h at 600°C) it appeared that the given TEX-value of the glassfibres is quite accurate. Hence, the variations in weight are totally due to variations in the weight of the nylon. In most applications this weight variation will not have a substantial impact on the total weight of the final product. A perhaps more serious result could be local deviations of the optimum fibre volume content, which in turn could locally result in poor matrix dominated properties (interlaminar shear strength, peel strength, chemical resistance). Since the fibre volume content of the FIT-material is very low, this hazard is not likely to occur.

For the calculations of the fibre volume content, an average weight per unit of length is used. The results are given in table 2.

<table>
<thead>
<tr>
<th>fibre</th>
<th>weight [grams per meter]</th>
<th>[% of total weight]</th>
<th>fibre volume- percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FIT</td>
<td>glass</td>
<td>tube</td>
</tr>
<tr>
<td>FIT 320/12</td>
<td>0.79</td>
<td>0.32</td>
<td>0.38</td>
</tr>
<tr>
<td>FIT 1200/12</td>
<td>2.09</td>
<td>1.20</td>
<td>0.49</td>
</tr>
<tr>
<td>FIT 320/6/11</td>
<td>1.04</td>
<td>0.32</td>
<td>0.25</td>
</tr>
</tbody>
</table>

* used specific weights$^{33}$

glass: 2.58 g/cm³
nylon 12: 1.01 g/cm³
nylon 11: 1.04 g/cm³
nylon 6: 1.13 g/cm³
From table 2 another remarkable fact with regard to the impregnation can be seen, e.g. a large difference in glassfibre-content considering the three types of FIT-material.

Since the specific strength and stiffness (the strength and stiffness per unit of weight) of a composite material depend strongly on the fibre volume content the material properties will differ accordingly with variations of this parameter. In this context it is recommendable that the fibre volume content of all grades is increased and equalized, the last also in axial direction of the individual fibres.

The differences in the weight-contributions of the extruded tubes of the diverse FIT grades are also noteworthy. In principle, an optimum value for the weight ratio tube/powder will exist, which depends partly on the method of heating. This will be discussed later.

3. Experiments conducted on FIT-material.

In the following the experiments conducted on the FIT-material will be described. Applying the filamentwinding technique (see fig.2) a number of flat test specimens (of FIT 320/6/11, and FIT 1200/12) has been produced using two different approaches.

1: FIT-material
2: press-plate
3: winding mandrel
4: by-pass pipe with hot air gun
5: guidance eye moving in X/Y-direction
6: filamentwinding bench

Fig.1: The winding process of the flat laminates using FIT material.
1. The fibres were wound 'dry' (e.g. without applying any heat) on the plates and consequently pressed at 4 bar during 20 minutes at a temperature of 235°C and 200°C of the FIT 360/6/11 and the FIT XXXX/12 respectively. The specimen were then cooled under pressure. In this way UD (unidirectional) oriented laminates were obtained.

2. Before the fibres (FIT 320/6/11 only) were wound on the plate they were passed through a, by means of hot air guns, heated pipe in order to melt the nylon. However, the resin cooled down before the fibre touched the product, which resulted in a very poor quality of the test specimen. This was solved by pressing the plates afterwards under the abovementioned conditions. This time a crossply laminate (0°-90°-90°-0°) was made.

3. The fibres were wound 'dry' in a male-female mould which yields tensile-test specimen of 350x15xT mm (two times ASTM/ISO D3039) where 't' is the thickness depending on the amount of fibres, see fig.2. This mould has been placed in a hot press in which the specimen are consolidated under abovementioned conditions. During pressing a small amount of nylon was pressed out at the ends of the mould resulting in a somewhat higher fibre volume content than calculated for the 'dry' fibre. Where appropriate these values are also mentioned.

Tensile tests.

Both the UD- and the cross-ply laminates were tested with respect to stiffness and strength. The equipment used for this purpose was the Mohr und Federhaff testbench and an extensometer coupled to an XY-plotter. The specimen (175x15x2 mm for ASTM and 160x20x2 mm for the crossply laminates) were cut and aluminium tabs were bonded on the ends (using epoxy AF 163-2 adhesive film with carrier) to prevent slipping of the specimen in the grips of the testbench. The stress-strain curves were plotted from which the Young's modulus and the ultimate stress could be determined. The stress/strain-curves of both laminates showed a slight non-linearity, in such a way that the Young's modulus was maximum near zero load, gradually decreasing with increasing load. The specimen were tested up to ±80% of the ultimate strength resulting in an average 6% decrease of the Young’s modulus. After determination of the stiffness the specimen were loaded until failure, resulting in an elongation at failure of 2.0% for the UD-laminates and 1.3% for the cross-ply laminates. The results of the tensile tests, (with two values for the Young's modulus) are given in table 3.
Table 3: Results of the tensile tests on UD- and cross-ply laminates of FIT 320/6/11:

<table>
<thead>
<tr>
<th>laminate type</th>
<th>fibre volume content (%)</th>
<th>Young's modulus (at V=0) (MPa)</th>
<th>Young's modulus (at V%) (MPa)</th>
<th>Fy, max (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UD FIT 320/12</td>
<td>31</td>
<td>18500</td>
<td>17500 (230)</td>
<td>370</td>
</tr>
<tr>
<td>UD FIT 1200/12</td>
<td>37</td>
<td>29300</td>
<td>27800 (350)</td>
<td>2445*</td>
</tr>
<tr>
<td>UD FIT 320/6/11</td>
<td>19</td>
<td>16100</td>
<td>15200 (200)</td>
<td>250</td>
</tr>
<tr>
<td>360/6/11 (0°-90°)</td>
<td>19</td>
<td>8180</td>
<td>-</td>
<td>100</td>
</tr>
</tbody>
</table>

*slipping of the specimen occurred (if calculated with the law of mixtures with respect to the other results: approx. 500 MPa).

It must be emphasized that the results for the ultimate stresses \((\sigma_1, \text{max})\) are far below typical values for glassfibres. For instance, the widely used E-glassfiber offers an ultimate tensile strength of 3500 MPa, the G- or G2-glass fibre even 4600 MPa (values by Owens Corning Corp.). Using these values estimated tensile strengths for a 37% fibrevolume UD-laminate are 1295 MPa and 1700 MPa respectively. Due to splitting of the laminate in longitudinal direction as well as failure under the tabs the results will be lower than the optimum values, but even then the values are far too low. The question rises whether this degradation is a result of the impregnation method, or that the fibres used by ATOCHEM were of bad quality in the first place.

Microscopic examination.

When experimenting with the FIT-material it appeared that the fibres contain a considerable amount of air. The trapped air can result in voids when the FIT-material is consolidated without any precautions to prevent this forming of voids. Since such precautions were not taken when pressing the testspecimen, the presence of voids was very likely. Using a NEOPHOT 2 microscope the laminates were investigated in order to find the location and nature of these voids. In fig.2 a cross-section of the specimen (UD-laminate) is shown. The individual FIT-fibres can be distinguished very clearly. It seems that there is not much air enclosed between the single glassfilaments. The enlargement of the picture however is only 25 times, hence very small voids (5 to 10 \(\mu\)m) can not be recognized. Between the individual FIT bundles large voids can be seen.

![Fig.2: Consolidated FIT (25 times).](image-url)
These voids could be the result of a clustering of the air coming out of the tubes. Another reason could be an insufficient tension on the fibres during winding. In any case this phenomenon must be nullified in order to achieve optimum results with regard to mechanical, physical and chemical properties of the product made from FIT-material.

4. Filament winding experiments.

Using a NC filamentwinding machine some experiments have been done to investigate the processability of the FIT-material. In cooperation with ATOCHEM some tests were carried out in order to filamentwind a layer of FIT-material on a nylon tube (PA 12), (see fig.3). A program was written to obtain various angles of the fibres with respect to the axis of the tube: eg. circumferential winding (±90°) and helix winding (±30° and ±60°). The exact angle for circumferential winding depends on the 'smeared out' width of the bundle of filaments, hence this angle will vary accordingly with the type of material used.

![Fig.3: Cross-section of tube with wound FIT-material.](image)

As mentioned before, the first experiments were not successful because of the composition of the FIT 360/6/11 material. Excessive heat, necessary for melting the powder in the fibres resulted in an oxidized surface of the product. After changing the material to FIT 360/12 a number of parameters has been investigated. In the following this will be discussed. The set-up is given in fig.4.

![Fig.4: The set-up used for filamentwinding experiments.](image)
- Guidance eye.

When circumferential winding the fibre is almost straightly passed through the guidance eye. Therefore, no problems occurred in the first tests. When helix winding however, the resin was scraped of the fibre due to the friction between the guidance eye and the fibre. Various types of eyes made of diverse materials (steel, Teflon) have been used. The best results were obtained with a ringshaped ceramic eye as shown in fig.5.

Fig.5: Guidance eye for best results.

- Heating method.

The only way to achieve an adequate packing of the fibres around the tube is to preheat the fibres before filamentwinding. Otherwise, (eg. filamentwinding the cold fibres and subsequent heating) the circumferential tension, accomplished during winding is annihilated. When heating the fibres before they touch the product, the fibres are ‘smeared out’ (see later) and, by choosing the appropriate conditions the FIT-material will melt to the nylon tube, giving a (desired) cohesive bonding between the tube and the FIT-material.

Hot air guns were used to preheat the fibre. A hot air gun was mounted on a pipe, (see fig.4). Earlier experience with the aramid-fibre-FIT should justify the use of this method. During the tests with glass-fibre FIT however, it appeared that the temperature could not be adjusted to any level to obtain an acceptable result. If the temperature of the air in the pipe was raised high enough to melt all the nylon of the FIT-material, the outer surface of the fibre started to oxidize: Lowering the temperature resulted in a poor impregnation, which is a large deficiency in composite materials.

If a continuity of the hot air heating method is wanted, the question rises whether an oxidized (brown) surface of the product is acceptable. A possible reduction of the oxidizing process can be realized by reducing the amount of air which passes through the pipe. In fact, the heating can be done by passing the fibre through a tube-like oven. Whether the capacity of such an oven will be enough to heat the fibre with acceptable speed needs to be investigated.

Other possible ways to prevent oxidizing can be the use of hot-spot heating methods (laser) at the location where the fibre touches the product, or heating the mandrel by use of infra-red heating elements. The last suggestion was carried out, in addition of a reduced hot air heating of the fibres (see fig.4) during the last experiments, but as a result the nylon tube melted.
The distance of the elements was adjusted in order to lower the temperature at the tube, but at a certain point no effect could be distinguished anymore, while just before this point the tube still melted. Fig. 6 shows a microscopic photograph of a cross-section of the tube and the layer of FIT-material. Clearly visible are the large voids in the nylon tube and the smaller voids in the layer of FIT-material. (The large voids in the nylon tube could be the result of vaporized water, because the tubes were not dried before the experiments.)

![Cross-section of an overheated nylon tube.](image)

As can be understood from the above, the major problem of the experiments concerned the fact that the temperature could not be raised high enough to obtain a thorough impregnation of the glassfibres, without jeopardizing the tube material (see fig. 6). Tests will be carried out soon using a hot mandrel and again hot air guns to preheat the FIT-material. In the future also laser-heating methods will be investigated.

- **Winding speed.**

It is obvious that the speed with which the fibre passes through the hot pipe directly influences the temperature of the fibre. Particularly when helix winding the winding speed needs to be adjusted in such a way that the fibre passes through the hot-airpipe with a constant speed.
Another restriction on the winding speed is given by the viscosity of the hot nylon, as it has been observed with regard to the spreading of the fibre. Of course the spreading is also influenced by the temperature of the fibre and product (mandrel), but it appeared that a constant, relative low windingspeed and a constant, relative high fibretension (250 g) are also main parameters with respect to the quality of the product.

All this needs to be investigated more thoroughly in order to obtain an acceptable filament winding production process with FIT-material.

5. Conclusions and recommendations.

The conclusions of the preliminary investigation of the glass-FIT material are:

- The quality of the material needs to be enhanced, particularly on a number of issues:
  - A more constant amount of nylon with regard to the individual FIT-fibre in axial direction, for all grades.
  - An increasing of the fibrevolume percentage, hence lesser matrixmaterial, likewise for all grades. A desirable value for structural use is 60% (depending on the application).
  - The prevention of locked air in the fibres.

- A combination of PA 6 for the tube material and PA 11 or PA 12 for the powder could be the solution to the 'burning' problem which now exists in particular with FIT 320/6/11. The large heat flux necessary for melting the tube as well as the powder results in a burned, brown surface of the fibre and thus of the product. Recent developments show that this problem can be solved by a proper choice of the various parameters involved in the proces.

- The stiffness of the UD-tensile specimen do meet the expectations for this kind of material. However, the values for the tensile strength are quite inadequate. The fibre volume content does affect the mechanical properties to a great extent, but even when this issue is enhanced the values will be too low. Very recent tensile tests conducted on a UD-oriented test-specimen made of FIT (with a fibre volume content of 50% by scraping of the resin) yielded a tensile strength of 1000 MPa. A typical value for this kind of material should be around 1700 MPa. Since the stiffness of the material does meet the expectations the disappointing tensile strength could be caused by a 'rough' handling of the fibres during the impregnation technique or the application of low quality glassfibres.

Within the scope of this report some recommendations are given. A lot of research has to be done on this material, on various topics. The explicit advantages of the use of nylon as resin material with regard to mechanical, physical and chemical properties can be investigated.
The experiences with the filamentwinding process showed that also in the field of processing a number of problems still has to be solved, in particular the heating of the material. Part of the problem of a burned surface of the fibre is a result of the hot-air heating method. Other means of heating (laser technology, induction, tube-ovens etc.) should be investigated in order to prevent this problem.

Finally, it would be very worthwhile with respect to application in aerospace technology if a FIT-material could be produced featuring aramid- or carbonfibres preimpregnated with high performance thermoplastics like PEEK, PEI, PAI PS or PPS.

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